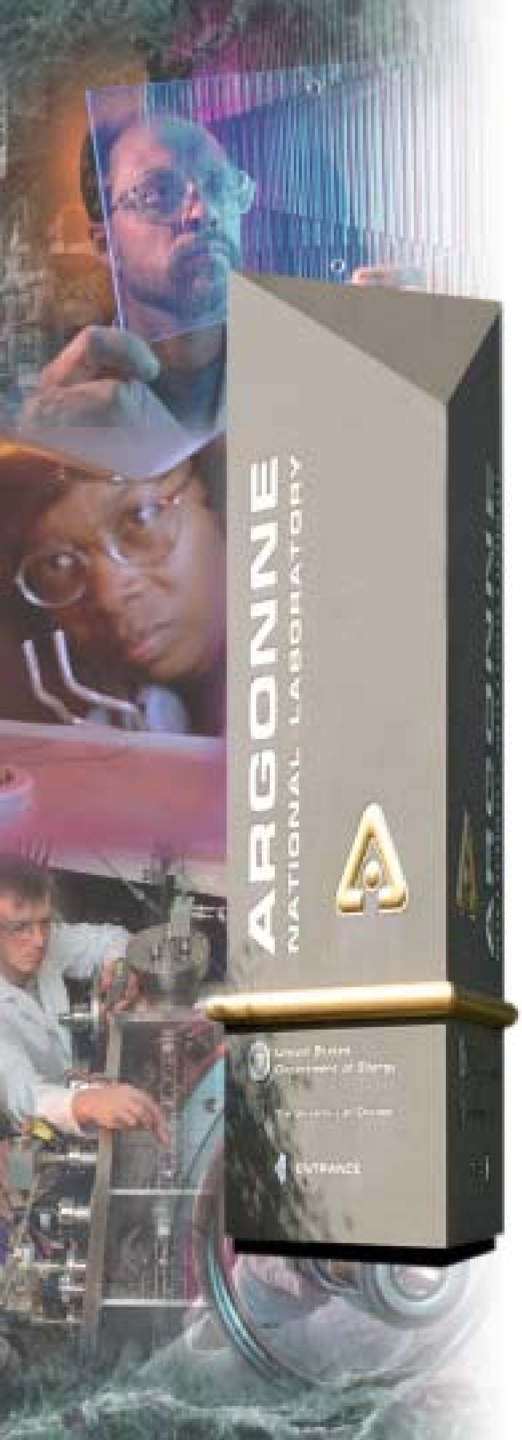


Nanoscience with X-rays

prepared for the

Scientific Advisory Committee for the Advanced Photon Source

by

Eric Isaacs

CNM Director

January 20-22, 2004

Argonne National Laboratory

A U.S. Department of Energy
Office of Science Laboratory
Operated by The University of Chicago

Talk Overview

- Intro – scientific case and some grand challenges.
- Nanoscience with x-rays – current and future.
- Experimental challenges.
- X-ray Nanoprobe and the Center for Nanoscale Materials.

Global Nanoscience Challenges

To explore novel phenomena associated with the interplay between spatial, physical and chemical length scales and proximity effects.

To transform the art of nanomaterial and nanodevice fabrication into a science.

To understand the ultimate limits of miniaturization.

To lay foundations for new technologies based on the principles of nanoscience.

Grand Challenges for Nanoscience with X-rays

- x-ray wavelength resolution.
- electronic and magnetic properties at the nanoscale.
- dynamics of single nanoparticle.
- structure of single macromolecule.
- coherent manipulation of nanoparticles.
- nonlinear x-ray processes.
- theory and modeling.

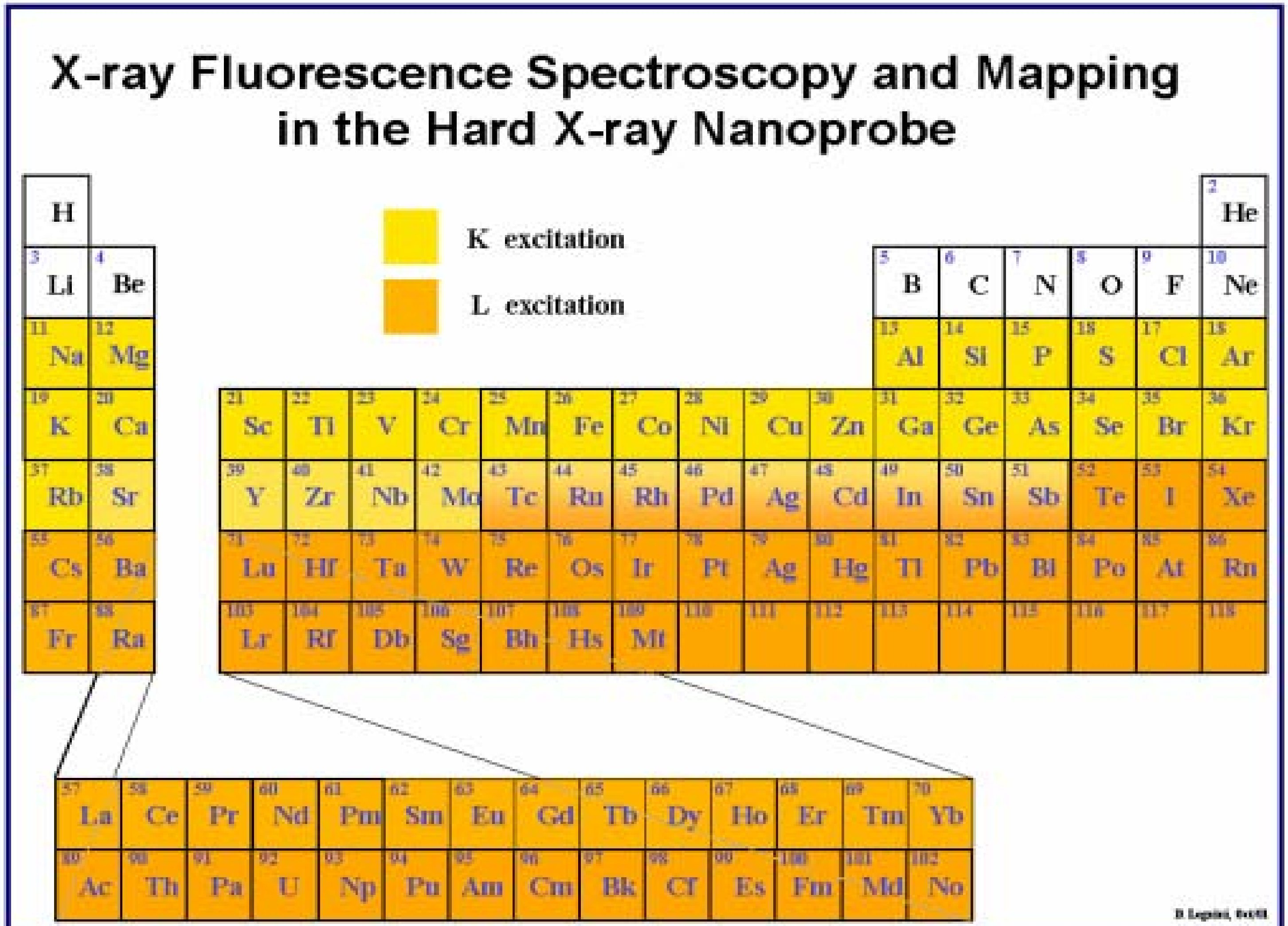
Scientific Case for Improved Hard X-ray Focusing

- Producing high-aperture focusing optics for hard x-rays has long been a "holy grail."
  - *There is no fundamental limit to focusing x-rays to spot sizes near their wavelength*.
- Enable new types of x-ray studies: nanoscale imaging, coherence manipulation, non-linear and high-field phenomena.
- Takes full advantage of high brilliance hard x-ray sources: APS, LCLS, NSLS-II.
- Improvements in fabrication capability provide new opportunities to push towards this frontier.

Nanoscale Imaging

- Applications in many fields: biology, geology, materials, chemistry, physics, nanoscience, ...
- Unique advantages of hard x-rays:
  - many contrast mechanisms for atomic-scale structure
  - quantitative and sensitive
  - three modes: scanning probe, full-field, coherent diffraction.
  - penetrating nature allows studies of “buried” features, in situ studies in fields, environments, real-time studies of dynamics

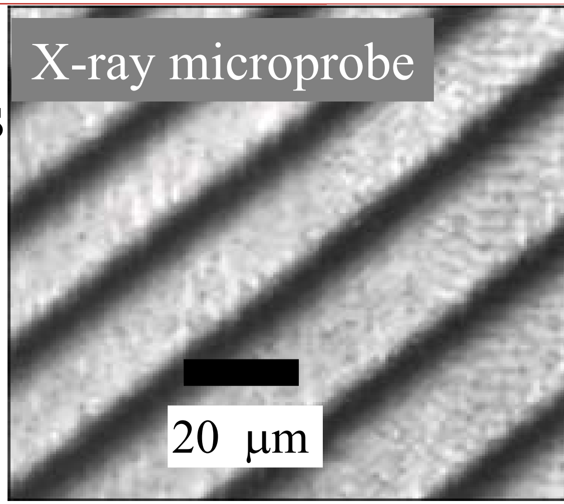
Hard X-rays Access Most of Periodic Table



Advanced Materials Research

substrate interactions and strain in films

P. Evans, et al. (2001).

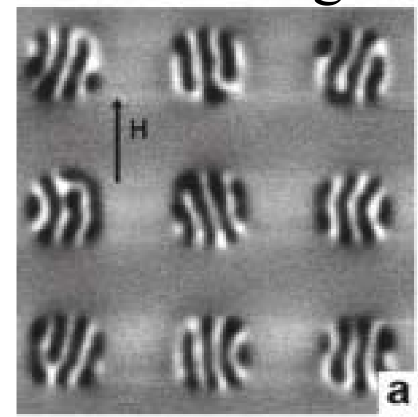


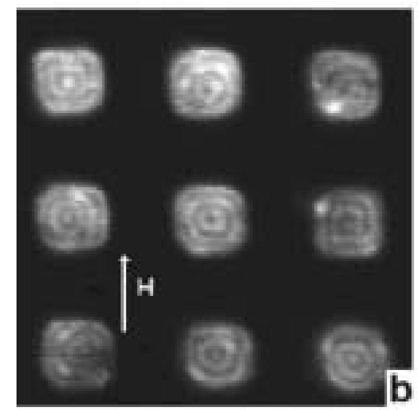
$BaTiO_3$ films, 90° domains

confinement

Co dots

MFM image



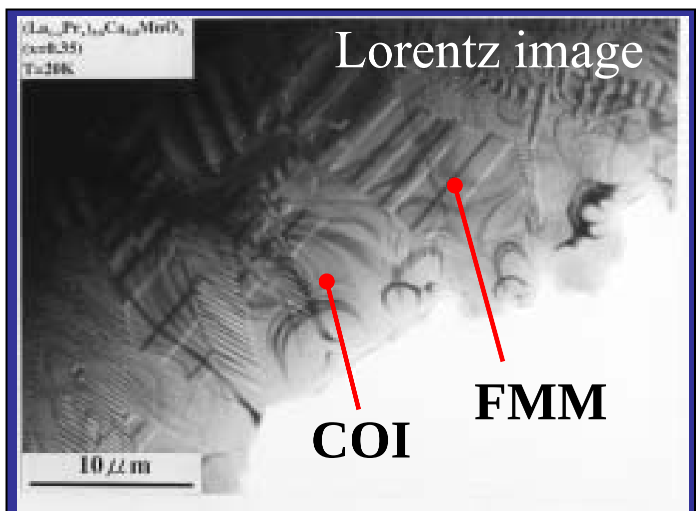


1 μm

M. Hehn, *et. al.*, APL **71** 2833 (1997).

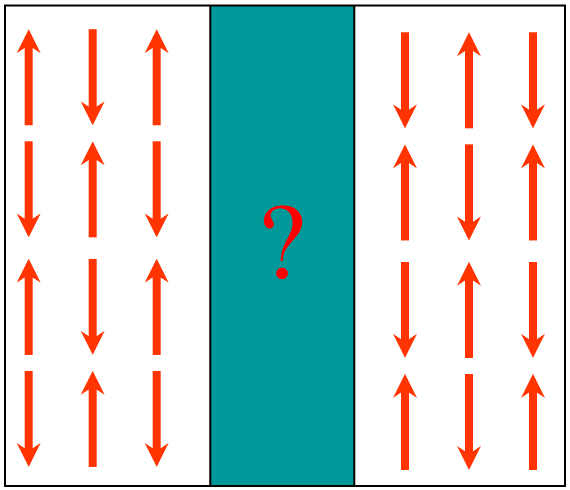
competing ground states, multiphase

C.H. Chen, et al., Nature (1998)

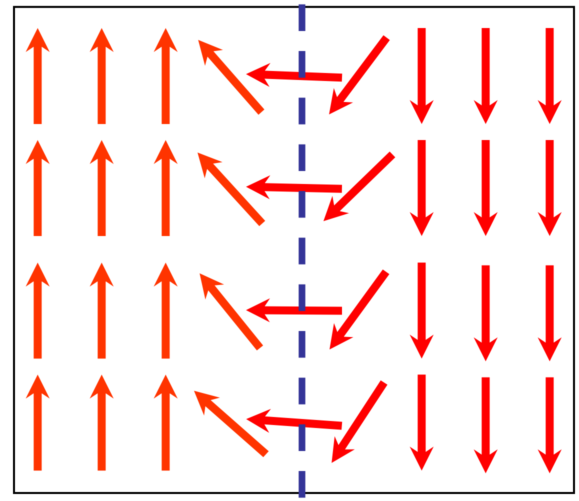


Physics of Domain Walls …

antiferromagnet



ferromagnet



Fundamental science

high T_C (e.g., striped phases)

CMR, quantum critical phenomena,…

Technological importance

hard magnets, recording medium, eg.,

non-volatile memory (M/FRAM), etc..

Length scales

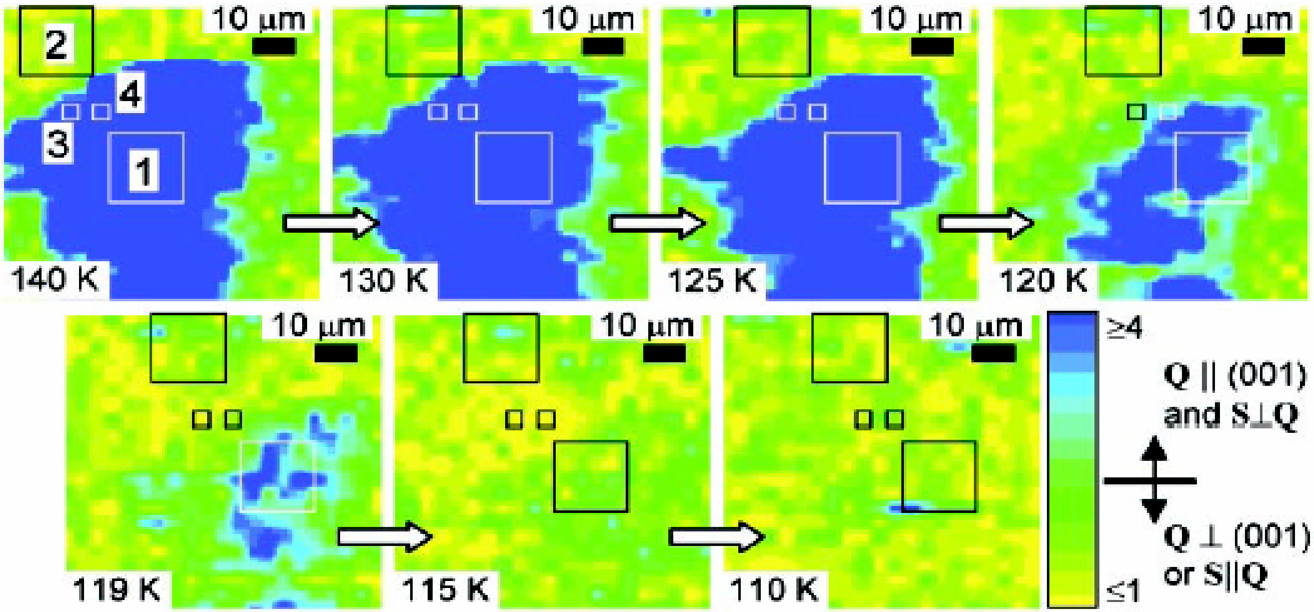
Bloch wall (FM)

$$\sigma_{\omega} \sim 2\pi\left(KJS^{2}/a\right)^{1/2}$$

nm – μm

AFM ???

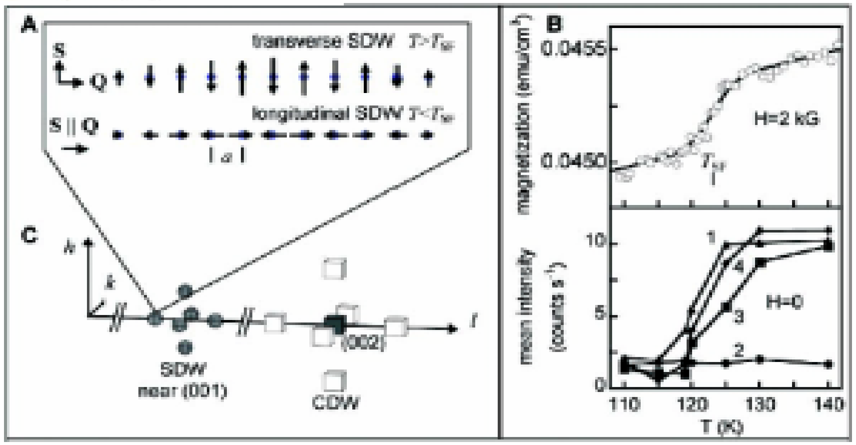
Antiferromagnetic Domain Evolution in Chromium



- **P.G. Evans, et al., *Science* 295, 1042 (2002).**

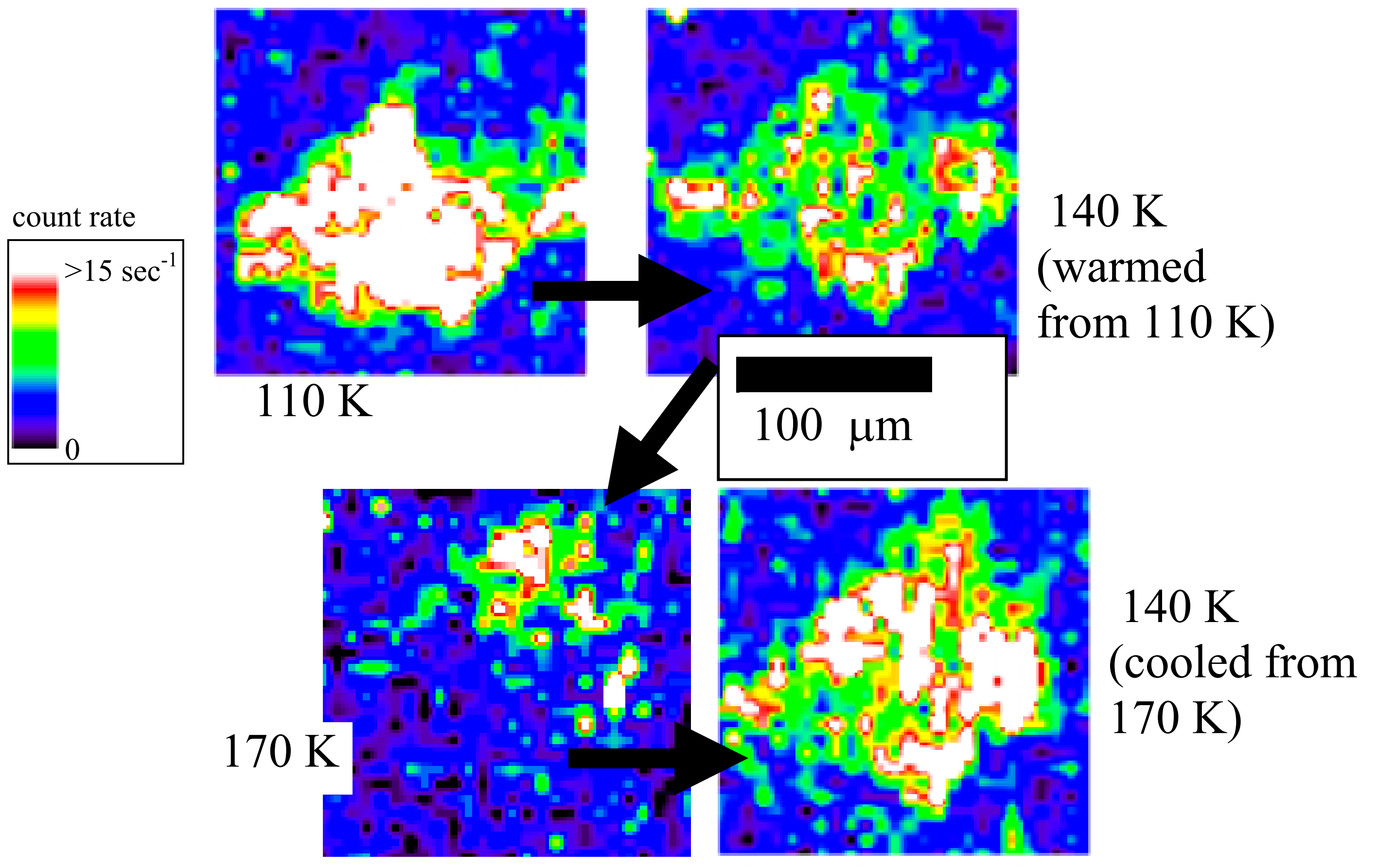
Spin-flip transition T is non-uniform within domain

- Magnetic diffraction contrast allows imaging of regions with different magnetic order



Thermally Activated Domain Wall Motion

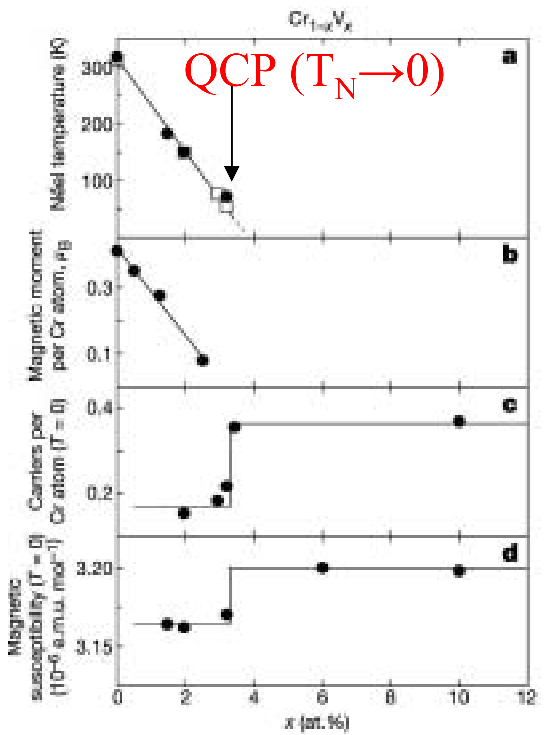
thermal hysteresis in Cr



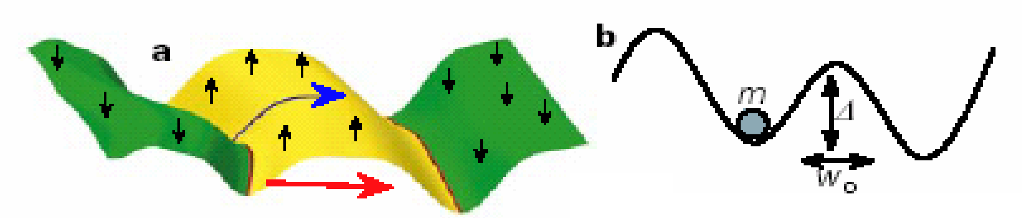
Domain Wall Dynamics in $Cr_{1-x}V_x$

Can we observe cross-over into quantum regime?

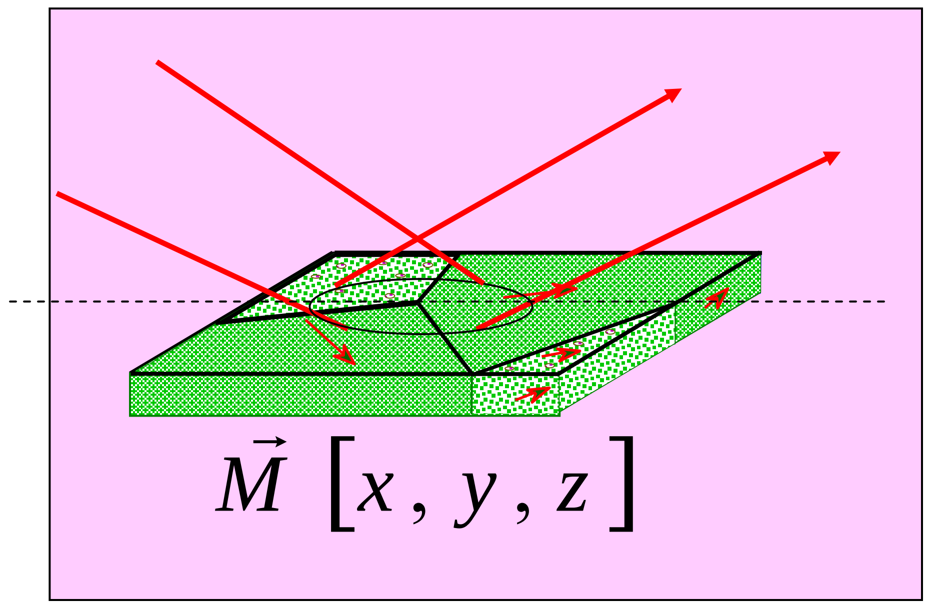
$T_N \rightarrow 0$ with x (or pressure)



A. Yeh, et al., Nature **419**, 459 (2002)

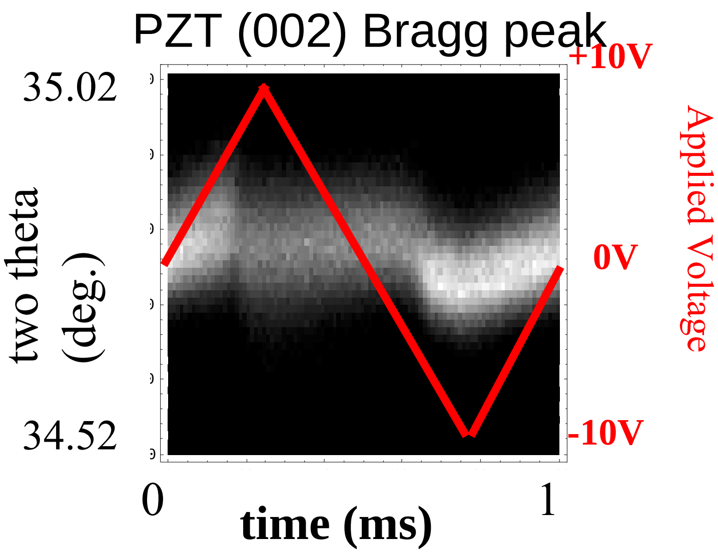


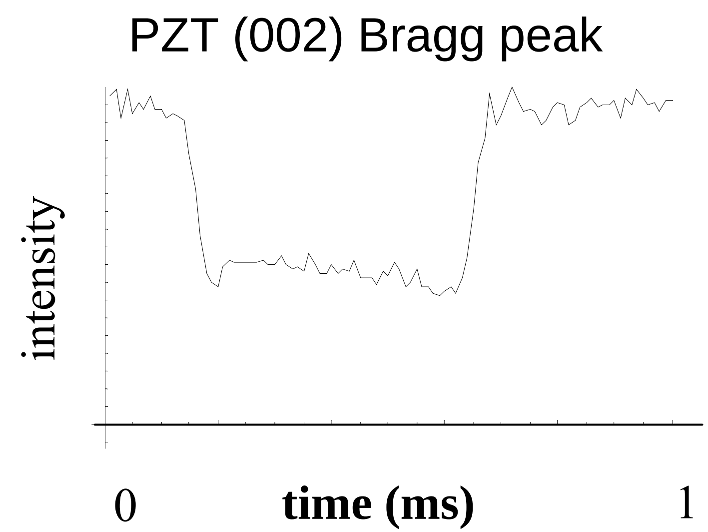
Domain wall (spin) tunneling

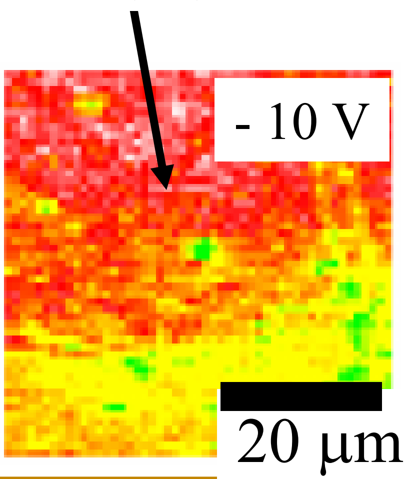


Polarization Dynamics in Ferroelectric PZT

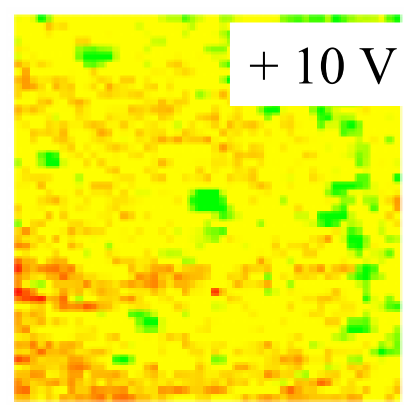
Paul Evans, et al.







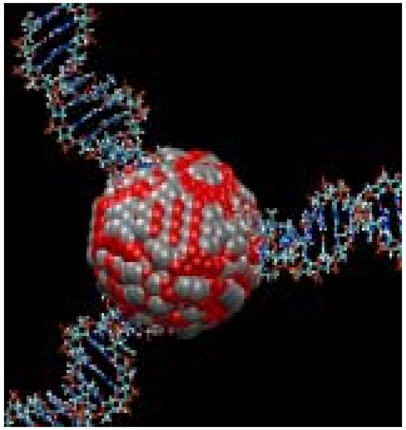
scanning probe images of (200) Bragg peak in PZT device.



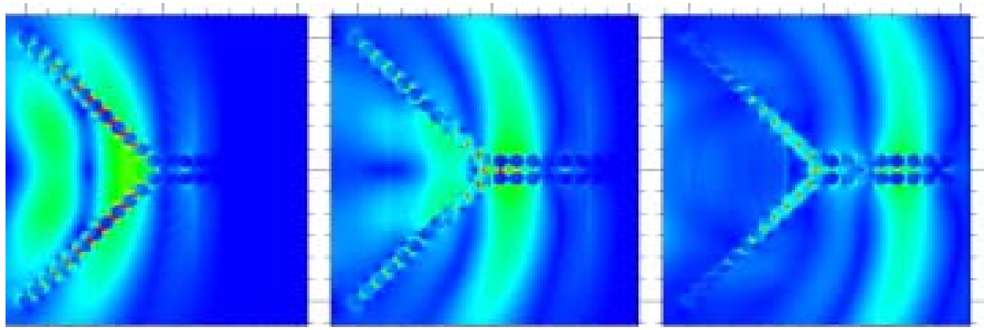
Dynamics on the Nanoscale

- Speed of sound 1 µm/nsec sets natural length and time scales.
  - 50 nm = 50 psec – natural limit at APS
- 10^7 photons/sec/pulse.
  - Can do ferroelectrics/magnetism.
- Can we do full-field imaging?

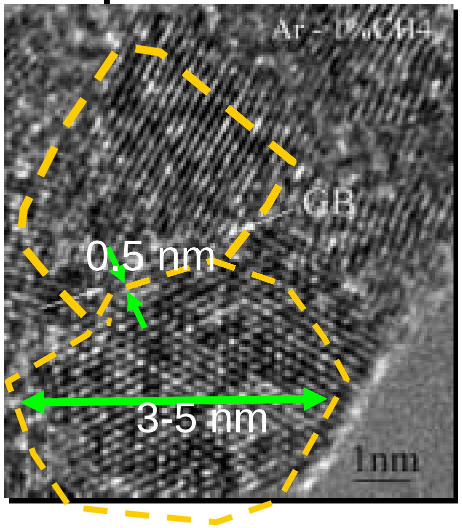
Structural, Magnetic and Electronic Properties of Nanoparticles

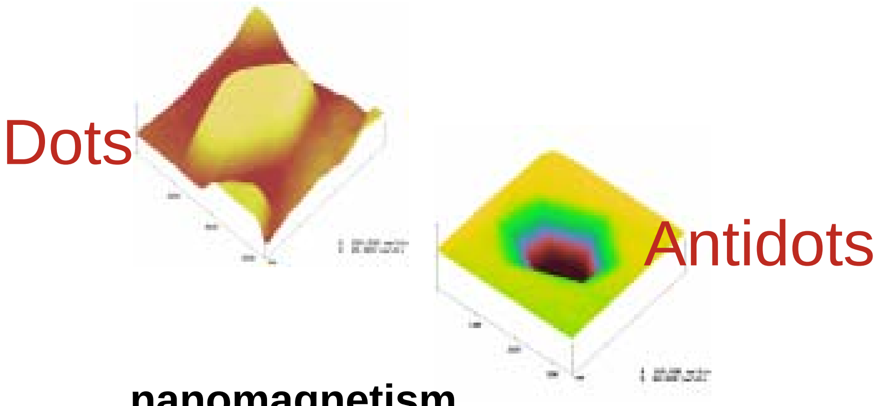


Novel functional nanocomposites



Sub-wavelength photon confinement/propagation

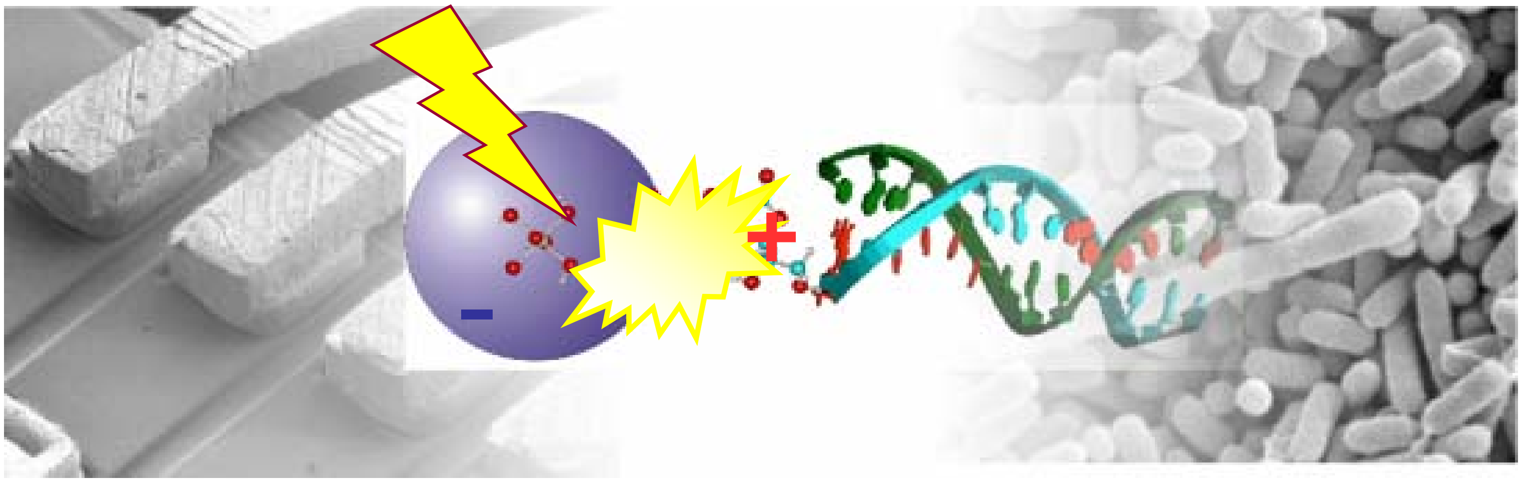




nanomagnetism

Bio-Inorganic Composite Materials

Create New Classes of Materials That Transcend the Biology/Inorganic Interface



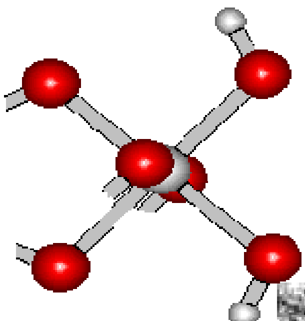
Light-induced DNA Chemistry

***Objective*: To design and synthesize nanostructured biocomposites that combine the unique features of biomaterials and inorganics**

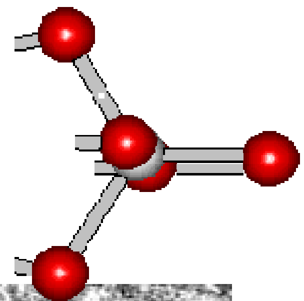
Interior vs Surface Sites Of Nanocrystalline Metal Oxides

Lin Chen
Tijana Rajh
Xiaobing Zuo
David Tiede

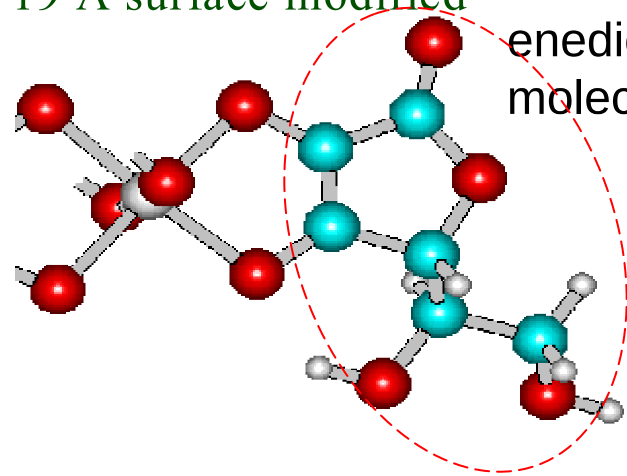
Octahedral
500 Å

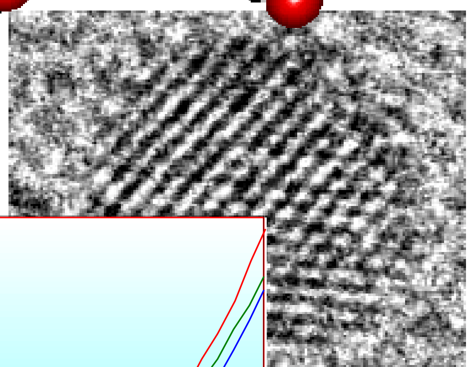


Square-pyramidal
19 Å

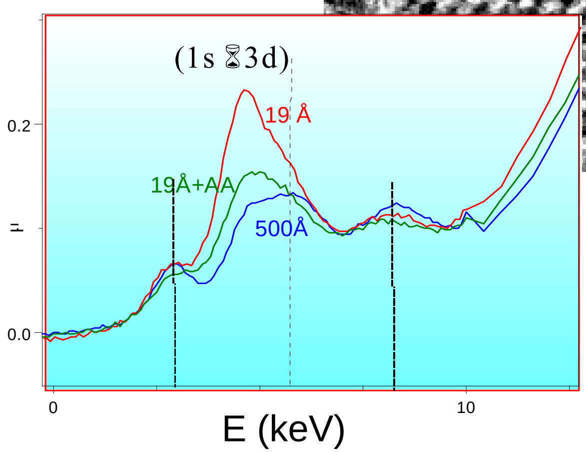


Octahedral
19 Å surface modified





NEXAFS

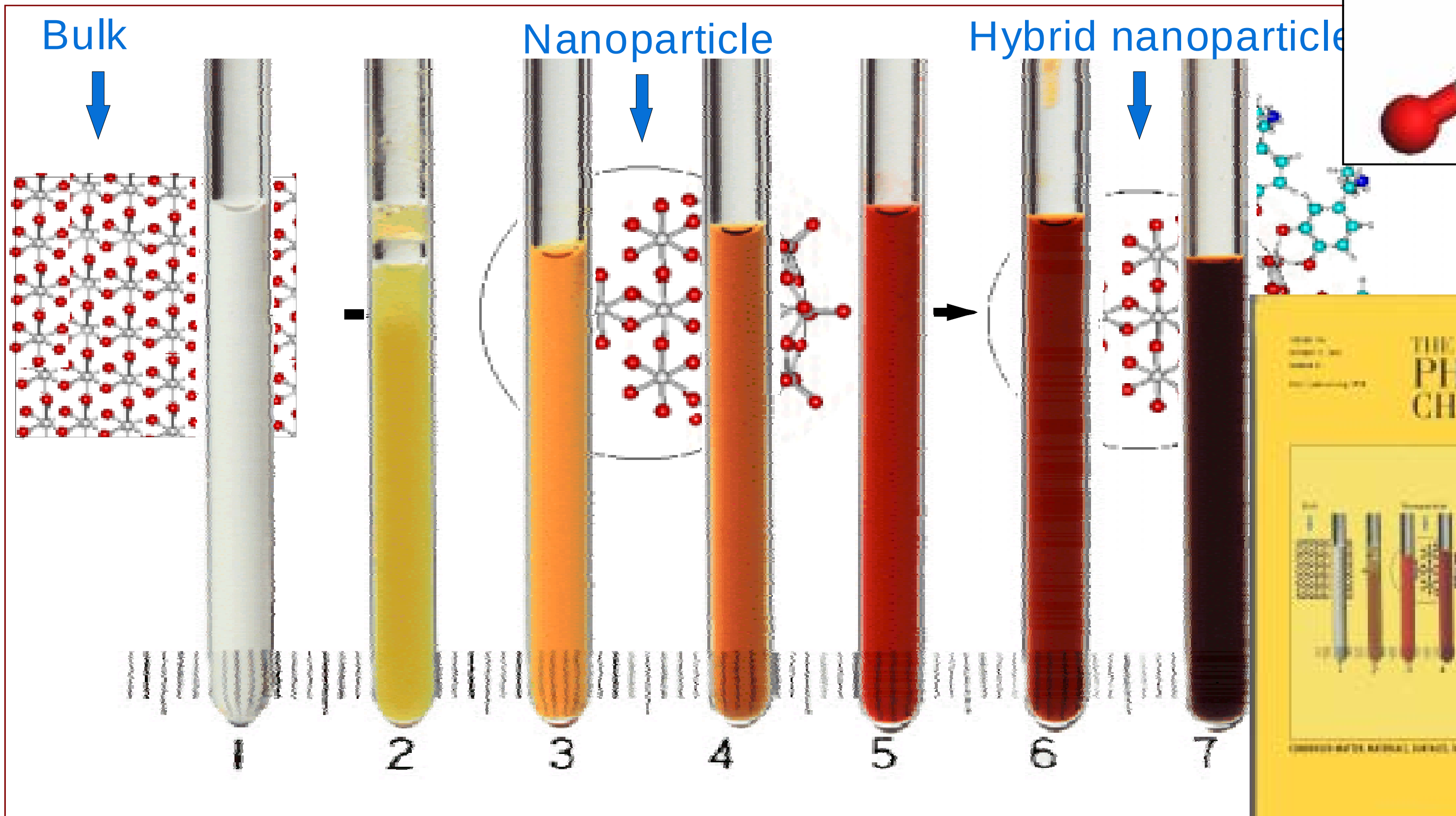


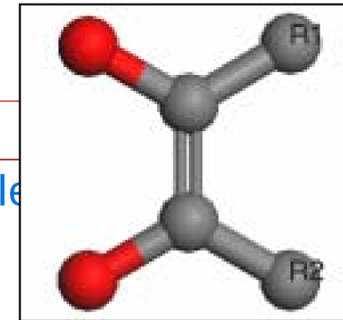
In nanosize regime (<200 Å) particles experience adjustment of coordination environment of surface sites

Different under-coordinated defect sites are the source of novel enhanced and selective reactivity of nanoparticles

Adsorption induced healing of the nanoparticle surface.

Engineering the Nanoparticle Interface- Enediol linkers

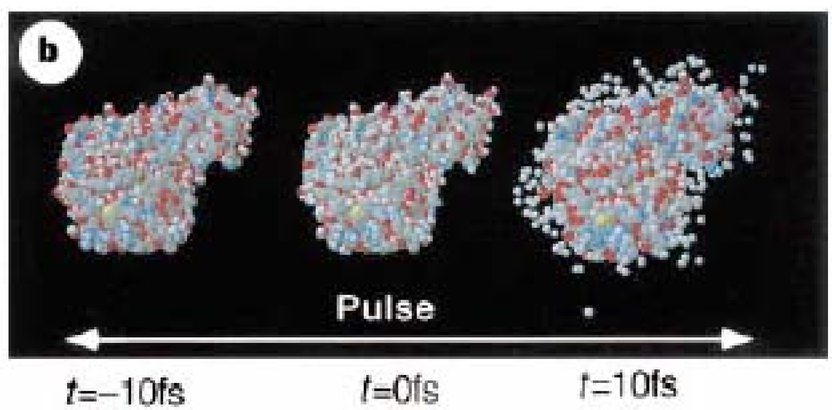


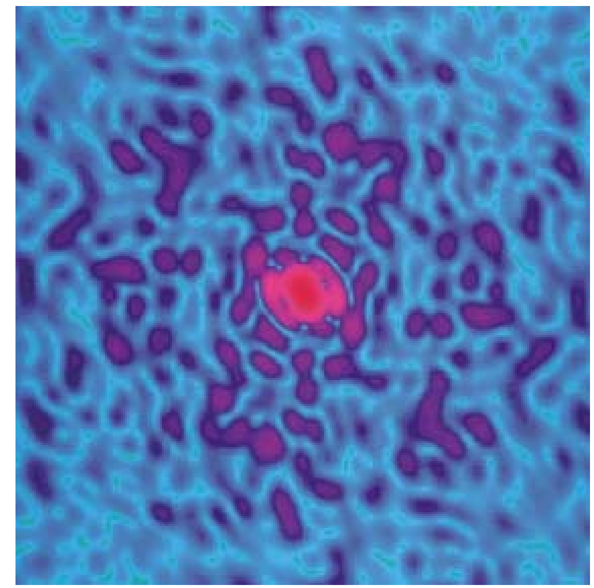


- Restructure surface atoms to resemble particle interior
- Mix molecular orbitals of linkers with inorganic conduction bands
- Bridge to bio-organic molecules

Atomic resolution imaging of individual nanoparticles and macromolecules.

- Collect speckle pattern using coherent diffraction with focused 100 fsec pulses (eg, LCLS).
- Invert mathematically to obtain structure.

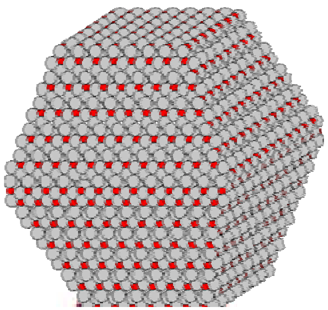




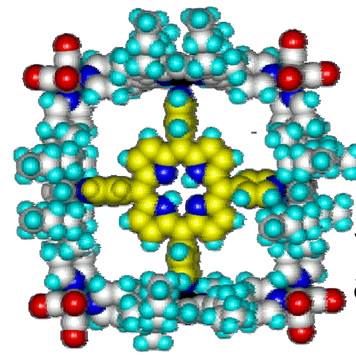
R. Neutze *et al.*, *Nature* 406, 752 (2000)

Imaging of individual nanoparticles and macromolecules at the APS

- Nanoparticles as small as 10 nm (~ 50,000 atoms) should be possible at the APS (Fuoss, et al.).



TiO_2



Synthetic molecular assemblies (J. Hupp, NU)

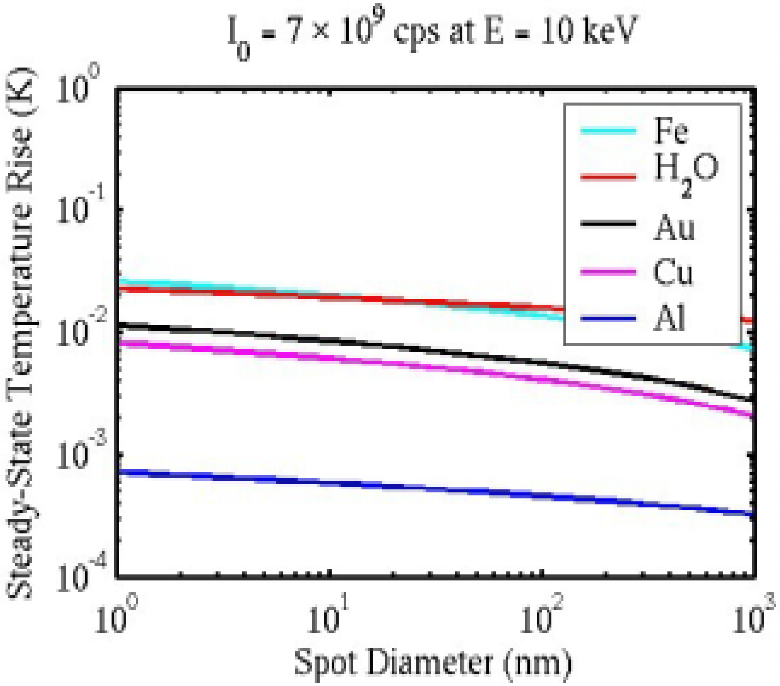
- Example: 10 nm Fe particle

$$\frac{d\sigma}{d\Omega} \sim 3x10^{-9} \quad \mu m^2$$

require > 10^{10} photons/sec into 10 nm spot.

Beam Damage Issues

- **Sample heating**
  - continuous source, e.g., APS
  - $I=7x10^9$ cps @ 10 keV
  - Large surface/volume ratio
  - pulsed source, e.g., LCLS
    - adiabatic heating, > 10^4 K rise.

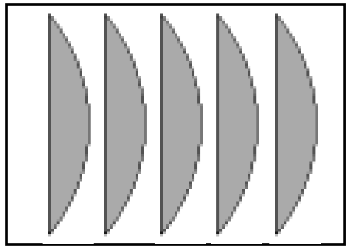


- **Photochemistry – organic/biological samples.**
  - damage threshold – 30 nm spot in 1 msec at the APS.

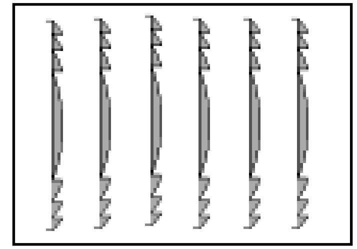
    (LCLS: $5x10^{13}$ cps into 100 um spot @ 8 keV.)

Vision: High NA Hard X-ray Focusing Optics

- Refractive:



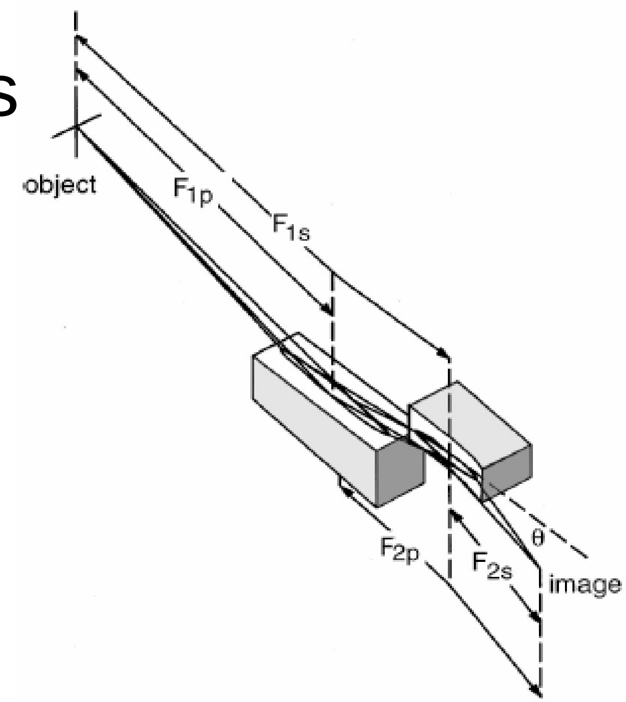
Compound refractive lens



Compound Fresnel lens for high NA

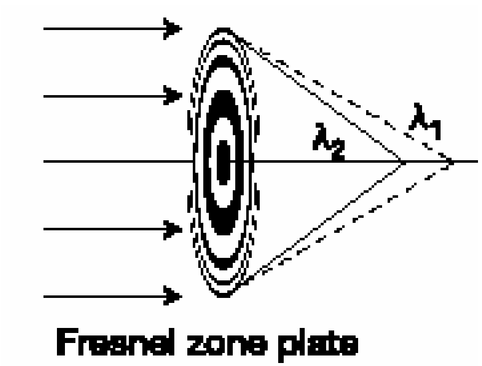
- Reflective: Kirkpatrick-Baez Mirrors

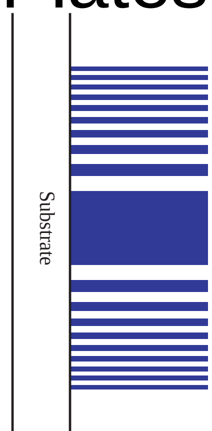
Figure by differential deposition, multilayer coated for high NA

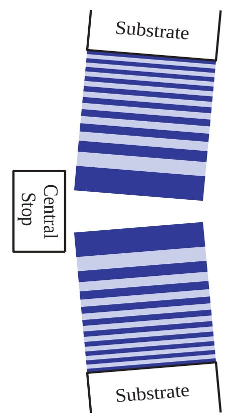


High aspect ratio, tilted zones for high NA

- Diffractive: Zone Plates







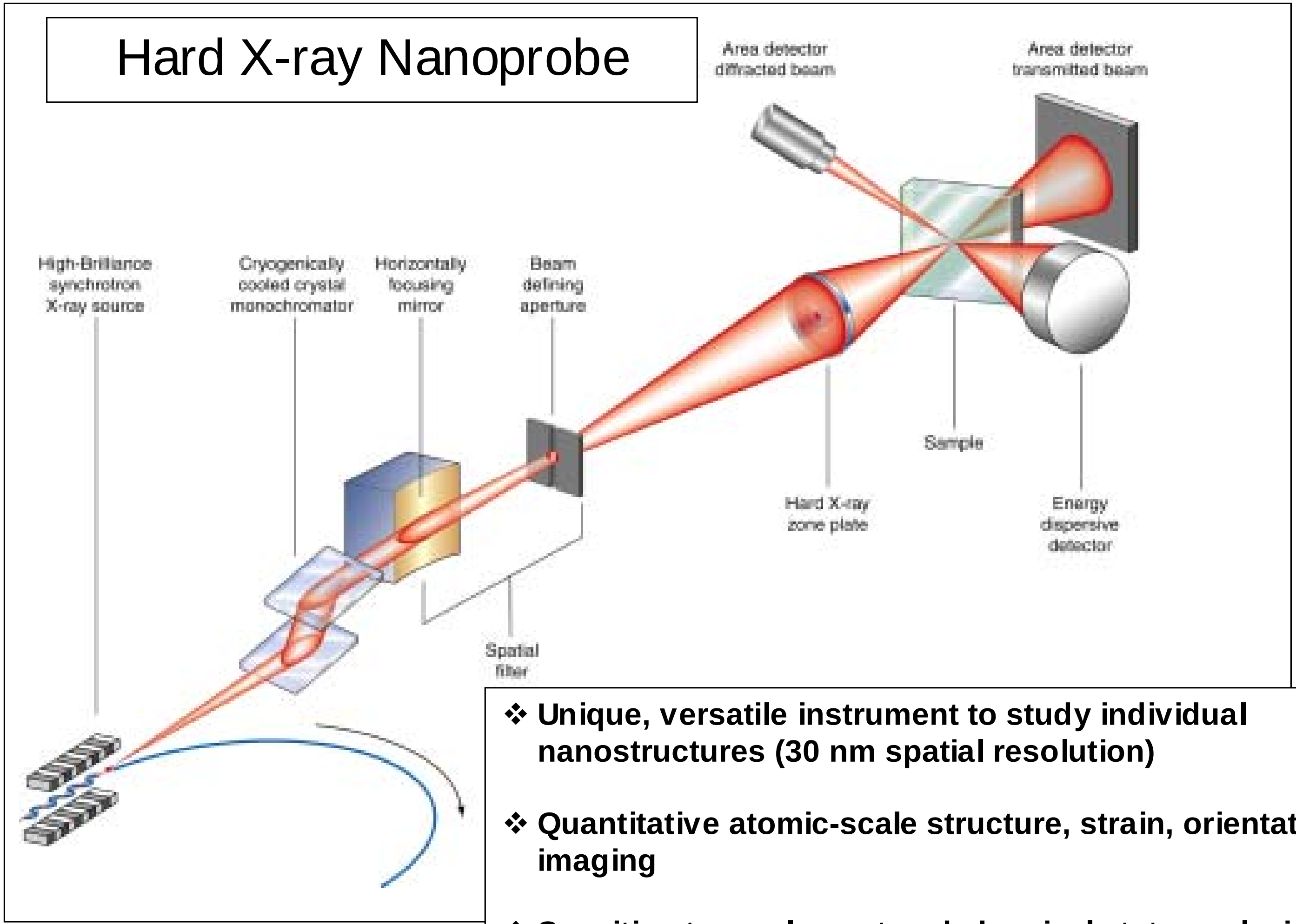
Lithographic zone plate

Transmission multilayer

The Ultimate Hard X-ray Microscope Workshop

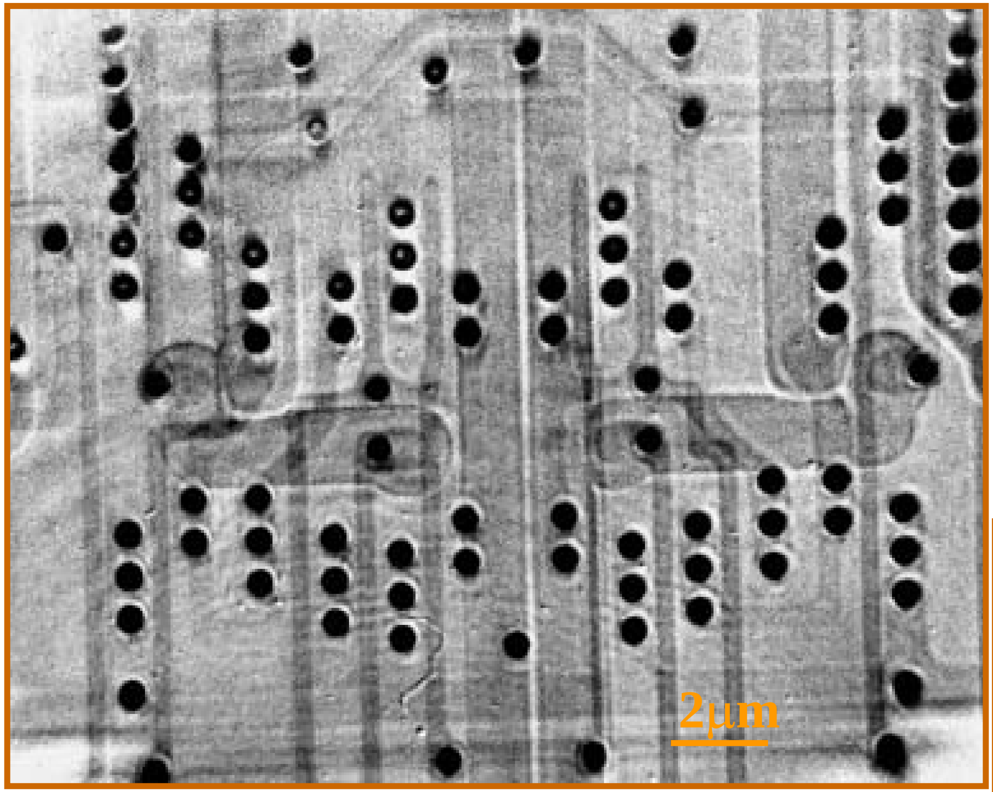
- Workshop at Argonne in June ’04.
  - Participation from Oak Ridge, Brookhaven, Argonne, Berkeley, Stanford, academia and industry.
- Articulate vision for ultimate hard x-ray microscope.
  - focus on large numerical aperture optics.
- Coordinate numerous smaller efforts, e.g., ORNL/ANL, ANL/Lucent, ANL/LBL, Xradia, etc..
- Provide 5 year roadmap for DOE.
- Need APS SAC support!

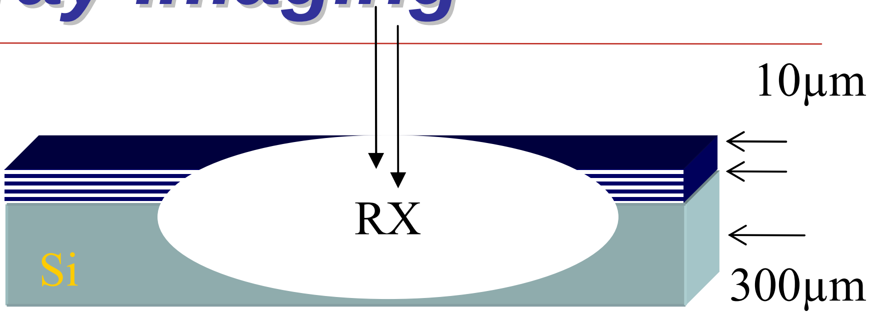
The Center for Nanoscale Materials Hard X-ray Nanoprobe



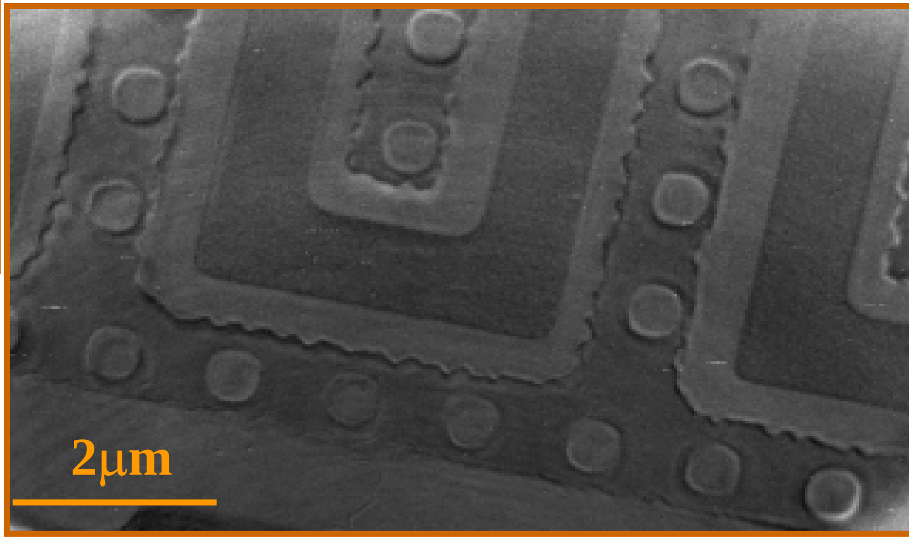
- ❖ **Unique, versatile instrument to study individual nanostructures (30 nm spatial resolution)**
- ❖ **Quantitative atomic-scale structure, strain, orientation imaging**
- ❖ **Sensitive trace element and chemical state analysis**
- ❖ **Operates in both scanning probe and full-field mode.**

Example of Full-Field X-ray Imaging





- Hard X-rays allow non-destructive imaging of buried structures, in-situ studies in fields, real-time studies of dynamics

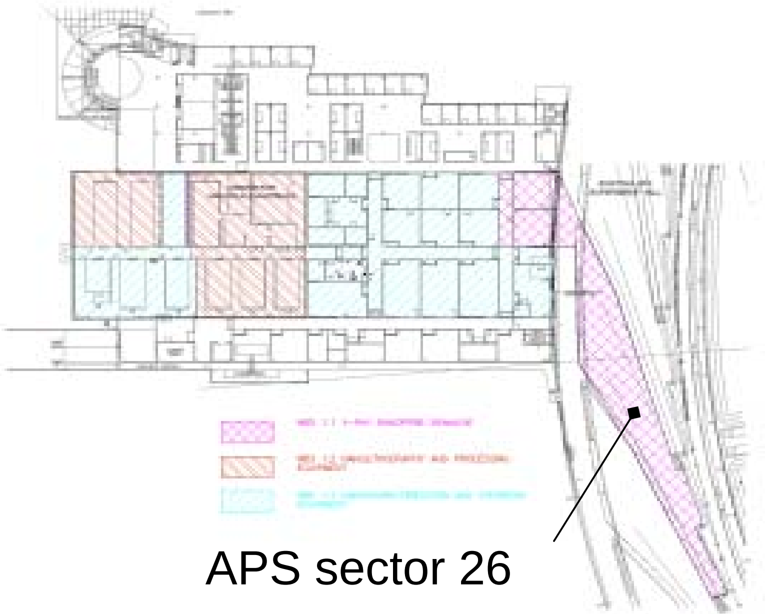


- E = 4keV
- Resolution ~ 80nm

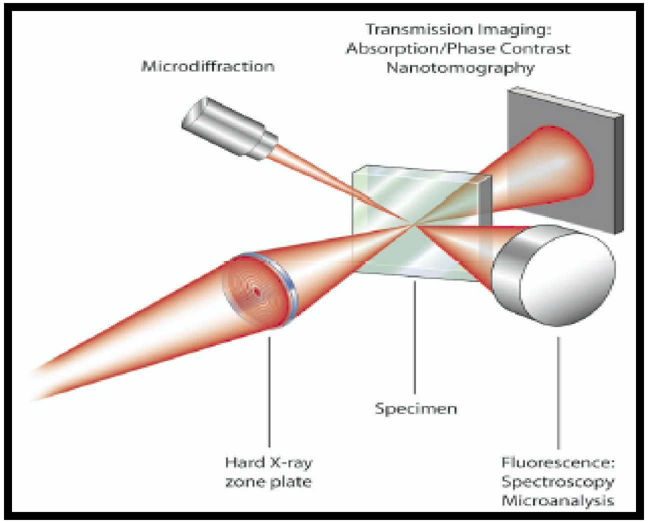
- Courtesy J. Susini, ESRF, Grenoble

CNM Hard X-ray Nanoprobe

- X-ray nanoprobe beamline: a unique imaging instrument
- Use high-brilliance APS source to produce world's highest resolution hard x-ray images.
- Powerful tool for nanoscience - can map density, elemental composition, crystalline phase, strain, texture, chemical state, atomic environment, magnetization.
- Adjacent to CNM building.
- Energy range 3 - 30 keV.
- Zone plate optics.
- Initial resolution goal: 30 nm.
- Initial operation FY07.



Center for Nanoscale Materials



World-class research facility at Argonne for tackling the grand challenges of nanoscience.

$ 72 M Federal/State Partnership

- ***transforming the art of nanomaterials to a science.***
- ***laying the foundations for future nanotechnologies.***